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DENSITY FUNCTIONAL BASED TIGHT BINDING STUDY OF C_2 and CN DEPOSITION ON (100) DIAMOND SURFACE

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ABSTRACT

A density-functional based tight binding method was used to study elementary steps in the growth of ultrananocrystalline (UNCD) diamond. It was shown previously that C_2 dimers are the dominant growth species in hydrogen-poor argon plasmas. Recent experimental evidence shows that nitrogen addition to the plasma profoundly changes the morphology of the UNCD film. CN species are believed to play a major role. Reactions of C_2 and CN molecules with reconstructed diamond (100) surfaces were studied. A single CN prefers an end-on attachment to a surface atom on the unhydrided (100) surface with its C end down. It is shown how further C_2 addition to the surface leads to CN-mediated diamond growth and how the CN species remain on top of the growing diamond layer.

INTRODUCTION

Diamond film growth from argon/methane plasmas produces ultrananocrystalline diamond (UNCD) with an average size of 3-10 nm.[1] Nitrogen addition to the plasma in the amount of 1% to 20% strongly influences growth and renucleation rates as well as the composition of the resulting films. These films have a range of unique mechanical and electronic properties, which are associated with small crystallite size and large number of grain boundaries.[2]

The renucleation rate in UNCD growth is several orders of magnitude higher than that in the conventional diamond synthesis from hydrogen/methane plasmas. Examination of plasma emission spectra detected a Swan band produced by carbon dimers.[3] This led to studies of diamond growth mechanisms on (100) and (110) surfaces using carbon dimers as precursors.[4,5,6,7] In contrast, hydrogen abstraction and surface reactions with hydrocarbons such as methyl radicals play a central role in the established mechanisms of conventional microcrystalline diamond growth.[8] On the basis of quantum chemical modeling of C_2 reactions with the unhydrided and hydrogen-covered diamond surfaces, it was proposed that reconstructed hydrogen-free surface sites can act as chemically active nucleation sites after dicarbon insertion.[5,6] Strongly exothermic reactions leading to diamond growth on unhydrided and monohydrided diamond surface were calculated as well. Subsequently, a growth mechanism on the (110) surface based on C_{2n} chain formation and coalescence was investigated using a density-functional-based tight-binding method (DFTB).[7]

In view of the strong modification of the growth process by nitrogen addition to the plasma, it is interesting to investigate the nitrogen role in the growth process. One of the common plasma species in this case is the CN molecule.[3] In the present paper we examine the interaction of the CN radical with the unhydrided diamond (100) surface using the DFTB method. Further, we study the concurrent adsorption of a CN molecule and several C_2 molecules to shed light on the modification of the growth mechanism.

THEORETICAL METHODS

The molecular dynamics calculations were performed using a density functional based tight binding (DFTB) method with self-consistent charges using the approach of Frauenheim, Seifert, *et al.*[9,10] The basis functions and the tight-binding matrix elements in this scheme are obtained from reference density functional calculations. A self-consistent charge scheme is based on the second order expansion of the density functional over electron density fluctuations. This term is expressed through Mulliken charges and calculated self-consistently at each simulation step. The self-consistent charge scheme is necessary to correctly take into account effects of surface polarization. The method has been applied successfully to diamond systems including studies of surfaces and diffusion problems.

The surface is modeled using a two-dimensional slab geometry with a thickness of 8 carbon monolayers. The bottom layer is saturated by a fixed monolayer of pseudohydrogen atoms, which do not interact with each other. The lateral extent of the periodic supercell is 4x4 unit cells. For all atomic structure calculations, we used the Γ-point approximation to sample the Brillouin zone.

For the adsorption studies, the molecules were placed sequentially on the surface and then their geometries were optimized using a conjugate gradient method. Calculations of the transition states between different geometries have yet to be performed. Previous studies indicated very low adsorption barriers of the order of 0.1 eV for C_2 depositions[7] in a similar environment.

RESULTS

The clean (100) diamond surface has two broken bonds per atom before reconstruction. The reconstruction leads to the formation of double bonds between nearest neighbors and results in a (2x1) pattern of dimer rows. The bond lengths of the C(100)–(2x1) reconstruction agree to 1% with first-principles calculations[11]. We obtain an optimized bond length of 1.40 Å for the surface dimer, at an equilibrium diamond lattice constant of 3.562 Å.

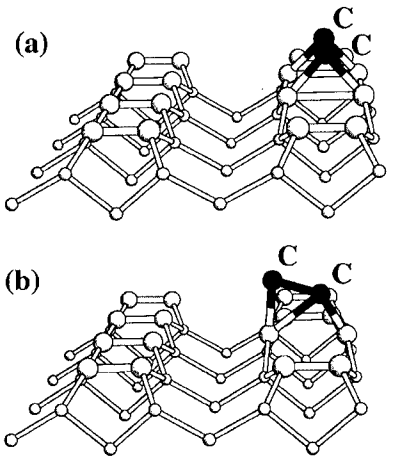

Figure 1. Stable geometries for C_2 adsorption on diamond (100) surface. Large circles denote surface atoms and black circles denote adsorbed atoms.

We have chosen the optimized geometries of an adsorbed carbon dimer on the reconstructed (100) diamond surface in its two most stable configurations as initial positions for the conjugate gradient search of CN stable configurations. The two positions for a C_2 molecule are shown in Fig. 1. The first position (Fig. 1a) is the most stable geometry for a carbon dimer. Both carbon atoms are inserted into C–C double bonds on neighboring surface dimers. This geometry is topologically identical to the surface dimer, and would thus constitute a growth site. The other position (Fig. 1b) represents a carbon dimer vertically inserted into just one surface C–C bond and strongly tilted by 73° relative to the surface normal. This configuration is believed to lead to the nucleation of a new diamond crystallite since the adsorbed molecule is highly chemically active.

As a first step in studies of the growth processes involving nitrogen, we have investigated the adsorption of a CN molecule on the reconstructed diamond (100) surface using the stable C_2 sites as initial geometries. Since CN is a heteropolar molecule, insertions with either the carbon or nitrogen end down in the second configuration were considered. The most stable configuration for a CN molecule, shown in Fig. 2, has carbon forming a bond with the surface carbon atom. This orientation is more stable than the one with the nitrogen end down. The configuration parallel to the surface with both carbon and nitrogen atoms inserted into adjacent surface dimer bonds (analogous to Fig. 1a) is unstable and relaxes to the geometry shown in Fig. 2. The tilt angle of the adsorbed CN dimer is 23°. The binding energy is 4.86 eV, which is smaller than 6.43 eV and 5.44 eV for carbon dimer in the configurations shown in Fig.1a and 1b, respectively.

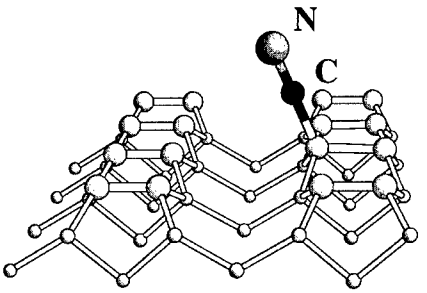

Figure 2. The most stable geometry of CN radical adsorbed on (100) diamond surface. Nitrogen is shown as a larger gray circle.

We have also considered the addition of C_2 dimers, as they would condense from the gas phase onto the surface in the presence of an adsorbed CN molecule with the intention to elucidate possible growth mechanisms. As a next step, we have simulated the adsorption of an additional C_2 dimer in the vicinity of a CN molecule on the surface. If the carbon dimer is attached beyond the immediate vicinity of the adsorbed CN molecule, i.e., on different sites, there are no chemical interactions between them.

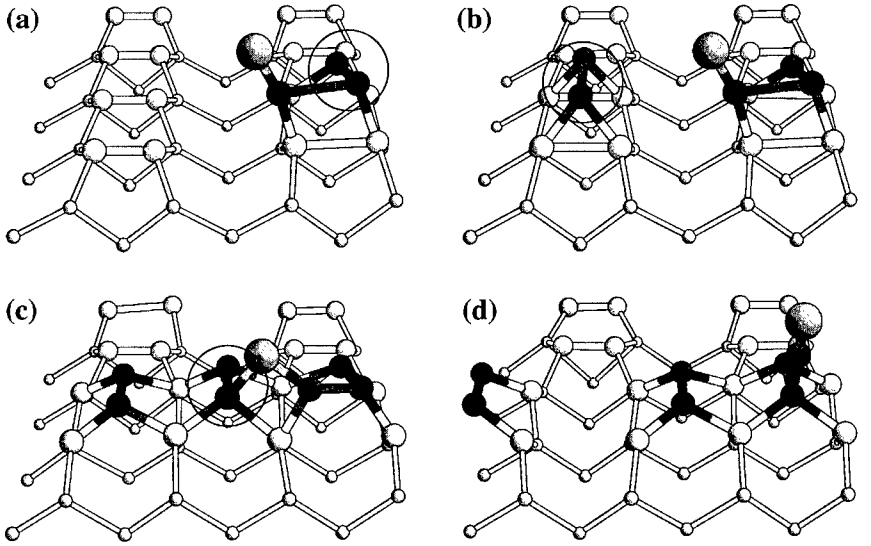

Figure 3. Steps in the CN-mediated diamond growth mechanism. The new adsorbed molecule at each step a)-c) is circled. The surface layer of the periodic supercell is shown larger. Atom notations are the same as in Figs. 1 and 2.

However, when the adsorbed C_2 shares a surface dimer with the CN molecule, as shown in Fig. 3a, the resulting complex is stable with a binding energy of 5.2 eV for the C_2 (10.1 eV for both adsorbates). One end of the carbon dimer forms bonds with the carbon atom of the CN molecule and the surface atom next to the CN adsorption site, whereas the other end is inserted into the adjacent surface dimer in the same fashion as in the configuration shown in Fig. 1a.

It is highly probable that there will be another C_2 adsorbed in the vicinity of the formed CN–C_2 complex, as shown in Fig. 3b. We will consider it as a next growth step although the order of these two events does not influence the reaction energetics and has no importance for the growth rate. This step is relevant in setting the stage for favorable adsorption of one more C_2 dimer that results in the structure shown in Fig. 3c. This geometry was optimized by the conjugate gradient method and turned out to be a local minimum. The binding energy for this C_2 attachment is 9.6 eV. This energy is larger than in the initial adsorption stages because the added C_2 leads to a more favorable tetrahedral coordination with its partners. Note that the nitrogen atom is attached to two carbon atoms in this structure. In order to probe the configuration space for other low-energy structures, a molecular dynamics simulation at 1000 K was performed starting from the structure in Fig. 3c. This led to the final structure shown in Fig. 3d. This structure is more stable than the starting configuration by 3.3 eV. Furthermore, one of the dimers performs a site hop. Examination of the structure shows that all adsorbed C_2's form part of the next layer of the growing diamond (100) surface. At the same time, the final configuration for the CN molecule is equivalent to the starting configuration shown in Fig. 2. As a net result, the CN dimer has moved onto the top of the next layer of the growing surface.

Thus, the CN-mediated growth mechanism, which is described above, consists of five steps: (i) adsorption of a CN molecule with its carbon end down; (ii) attachment of a C_2 dimer to the CN and the surface; (iii) independent attachment of another C_2 in the vicinity of the surface complex; (iv) bridging these adsorbates with another C_2 and formation of the second CN bond; and (v) low-barrier transformation of the structure to a more stable minimum with CN on top of the growing layer. All steps of this mechanism are exothermic.

The proposed mechanism provides initial insight into the growth process of UNCD. It can be inferred that nitrogen prefers to be located near the surface of the material rather than to be incorporated into the bulk. Indeed, the measured concentration of nitrogen in the material is very small (0.2% for 20% N_2 in the plasma) and it is thought to be located in the grain boundaries. Another result of this simulation is the conclusion that adsorbed CN species are much less reactive than the adsorbed C_2 species in Fig. 1b. This is due to the fact that N, which has a triple bond to C, would not interact with another molecule as easily as carbon that has two electrons available for chemical bonding in the latter configuration. The most reactive site after CN adsorption is the surface carbon atom next to the adsorbed CN molecule. Therefore, it is plausible that CN would block some surface sites that otherwise could be available for the nucleation of new crystallites and decrease the overall nucleation rate, while growth of the existing diamond lattice is promoted. Indeed, the experimental observation is that at higher nitrogen concentrations in the plasma the ratio of growth rate to nucleation rate increases, which leads to an increase in the crystallite size. Detailed investigations of other mechanisms of diamond growth from CN and C_2 precursors that would include a set of additional factors such as interactions of CN species, participation of hydrogen and reactions at other diamond surfaces are needed in order to fully characterize reactions involved in UNCD synthesis and provide opportunities to fully control the growth process.

CONCLUSIONS

Density-functional-based tight-binding calculations of CN radical adsorption on a diamond (100) surface gives a binding energy of 4.86 eV for the most stable geometry of the adsorbed molecule, which is a tilted vertical adsorption with the carbon end down. Further studies of C_2 adsorption in the vicinity of CN at the surface resulted in a growth mechanism with the CN molecule staying on top of the growing layer. These studies help to understand ultrananocrystalline diamond growth processes from hydrogen-poor plasmas.

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